Unusual line widths in the EPR spectra of copper(II) dithizonate

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Unusually wide lines have been found in the EPR spectra of copper(II) complex with dithizone (H_2Dz), in which the super hyperfine structure (SHFS) from ligand atoms was not resolved.

Dithizone (diphenylthiocarbazone, H_2Dz) is a widely used organic reagent for trace analysis, which can act as a monodentate or bidentate ligand.[1] The X-ray diffraction analysis of dithizone crystals showed that hydrogen atoms are localised at the terminal nitrogen atoms:[2]
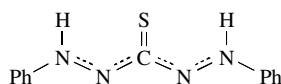
It is evident that π-electrons in the N–N–C–N–N system are fully delocalised. According to the valence bond method, the structural formula of dithizone is
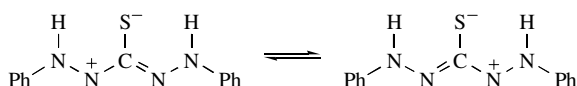
It was found that[3–5] dithizone produces bis-chelate complexes of the general formula $M(HDz)_2$, where M is nickel, copper or zinc, in which dithizone is bidentately coordinated through sulfur and nitrogen atoms with the formation of a five-membered metal-containing ring.

The copper complexes with dithizone were studied by EPR spectroscopy.[6,7] The EPR spectrum of $Cu(HDz)_2$ in dioxane at 293 K consists of four hyperfine structure (HFS) lines from unpaired electron spin interaction with copper nuclear spin [Figure 1(a)] and is described by the isotropic spin Hamiltonian (SH)
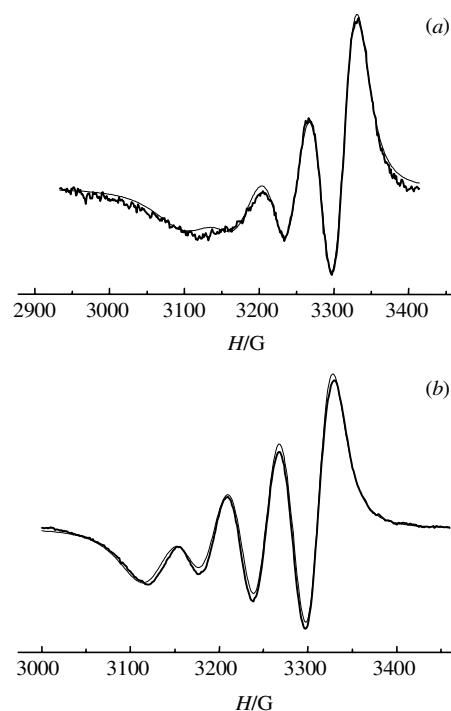
$$H = <g>\beta SH + <a_{Cu}>SI,$$

where β is the Bohr magneton, $S = \frac{1}{2}$ is the electron spin, $I = \frac{3}{2}$ is the nuclear spin of the two copper isotopes ^{63}Cu and ^{65}Cu (natural abundance of 69.1 and 30.9%, respectively) and H is the external magnetic field. The other SH parameters are presented in Table 1.

An unpaired electron is located at the $<d_{x^2-y^2}>$ orbital in square-planar copper(II) complexes with a d^9 electron configuration. The presence of sulfur atoms in the coordination sphere of transition element complexes usually results in significantly narrowing lines in the EPR spectra and hence promotes the resolution of SHFS from ligand atoms.[9] Thus, for instance, in copper complexes with bis(α-thiopicoline anilide) $\{Cu(\alpha$-tpa)$_2\}$, bis(8-thioquinoline) $\{Cu(tox)_2\}$ and thioacyl hydrazones of mono-

Table 1 Parameters for SH of copper compounds in solutions.

| Compound	Solution	$<g>$	$<a_{Cu}>/$ 10^4 cm^{-1}	$<a_N>/$ Gs	Reference
$Cu(HDz)_2$	dioxane	2.075	57	—	6, 7
	dioxane	2.068	55.5 59.5 (^{65}Cu)	—	This work
$Cu(\alpha$-tpa)$_2$	benzene	2.073	58	15.0	10
$Cu(tox)_2$	benzene	2.076	61	14.0	11
$Cu(tag)_2$	toluene	2.068	62.0 67.8 (^{65}Cu)	16.0	15
$Cu(HDz)_2$	chloroform	2.068	54.3 58.2 (^{65}Cu)	—	This work
$Cu(HDz,ddc)$	chloroform	2.056	74.2 79.4 (^{65}Cu)	12.1	This work

Figure 1 Experimental (thick line) and theoretical (thin line) EPR spectra of $Cu(HDz)_2$ (a) in a dioxane solution and (b) in a chloroform solution.

carbonyl compounds $\{Cu(tag)_2\}$, where the coordination sphere consists of two nitrogen atoms and two sulfur atoms [$trans$-N_2S_2], the lines in EPR spectra are narrow so that SHFS from two nitrogen atoms is resolved on several HFS components from copper atoms.[10,11,15] On this basis, one can expect that in the EPR spectrum of $Cu(HDz)_2$, in addition to four HFS lines due to copper nuclei, SHFS from two nitrogen atoms will be observed; however, as it was shown above, this is not the case. In the EPR spectrum of $Cu(HDz)_2$, not only SHFS from ligand atoms is not observed, but also the HFS from the copper nucleus is poorly resolved [Figure 1(a)].

The question arises: why a line in the EPR spectrum of square-planar $Cu(HDz)_2$ with the coordination sphere $trans$-N_2S_2 is widened so that the SHFS from two nitrogen atoms is not resolved. A reason may consist in low symmetrical distortions of the square-planar coordination sphere (for example, tetrahedral distortions resulting from the rotations of two metal-containing rings around the central metal atom, as well as the deflections of coordinated chelate rings).[12,13] Another reason may be that changes in the shape and size of a copper(II) dithizonate molecule affect the spin–lattice relaxation. This fact cannot be explained without further investigation into the structure of $Cu(HDz)_2$.

Table 2 Anisotropic SH parameters for copper compounds.

Compound	$g_{\|\|}$	A/cm^{-1}	$g_\perp$	B/cm^{-1}	$<a_N>_{\|\|}/$ G	$<a_N>_\perp/$ G	Reference
$Cu(\alpha$-tpa)$_2$	2.131	0.0154	2.037	0.0012	15.0	15.0	10
$Cu(tox)_2$	2.147	0.0172	2.036	0.0025	—	15.2	11
$Cu(HDz)_2$	2.145	0.0176	2.033	0.0026	17.2	16.5	This work
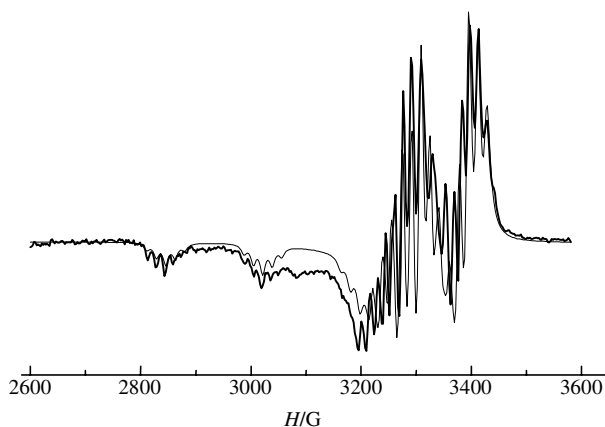
Figure 2 Experimental (thick line) and theoretical (thin line) EPR spectra of a magnetically diluted powder, $Ni(HDz)_2:Cu(HDz)_2 = 60:1$.

Reliable information on the structure of coordination compounds can be obtained by an EPR examination of magnetically diluted polycrystalline samples. For this purpose, we prepared monosubstituted copper(II), nickel(II) and zinc(II) bis-dithizonates and magnetically dilute powders of nickel and zinc dithizonates containing about 2% copper(II) dithizonate. The dithizonates were synthesised by the extraction method[1] using analytical-grade chemicals and chloroform as an extractant. To prepare the magnetically dilute compounds, 1 mg of copper dithizonate and 60 mg of nickel dithizonate (or zinc dithizonate) were dissolved in 20 ml of chloroform. The joint precipitation of complexes was carried out by slowly evaporating the solvent at a constant temperature.

The EPR spectra were recorded on a Radiopan SE/X–2542 radiospectrometer (9.45 GHz) at ambient temperature using DPPH as a reference substance. The copper(II) dithizonate concentration in solutions was 10^{-2} mol dm^{-3}. The computer-aided data processing was performed according to the published technique.[14]

The EPR spectra of $Cu(HDz)_2$ in dioxane and chloroform solutions are shown in Figure 1. The experimental SH parameters are presented in Table 1.

A comparison for Figures 1(*a*) and 1(*b*) indicates that the HFS from copper atoms in a chloroform solution is resolved better than that in a dioxane solution. However, the EPR lines are wide so that the SHFS from nitrogen atoms is also not observed.

Table 1 indicates that the isotropic parameters of SH are similar for the solutions of copper(II) compounds having similar coordination spheres [$trans$-N$_2$S$_2$]. It is well known[10,11,15] that $Cu(\alpha$-tpa$)_2$, $Cu(tox)_2$ and $Cu(tag)_2$ exhibit a square-planar structure of the coordination sphere in both a solid state and solutions. Thus, we can conclude that the coordination sphere of $Cu(HDz)_2$ in solution also has a square-planar structure. However, the EPR spectra of $Cu(HDz)_2$ in solutions exhibit an anomalously wide line.

The spectrum of the magnetically diluted polycrystalline Ni:Cu powder is typical of copper(II) compounds with the axial anisotropy of parameters (Figure 2), and it is described by the axially symmetrical SH

$$H = \beta[g_{\parallel}S_zH_z + g_{\perp}(S_xH_x + S_yH_y)] + AS_zI_z + B(S_xI_x + S_yI_y),$$

where $S = {}^1/_2$ is the electron spin; $I = {}^3/_2$ is the spin of the copper nucleus; A and B are the HFS constants from the copper nuclei in parallel and perpendicular orientations, respectively.

Table 2 summarises the anisotropic parameters of SH for $Cu(HDz)_2$, $Cu(\alpha$-tpa$)_2$ and $Cu(tox)_2$.

In the EPR spectrum of the magnetically diluted polycrystalline Ni:Cu powder, the SHFS of five lines is well resolved in both perpendicular and parallel orientations (Figure 2). The line intensity ratio is 1:2:3:2:1. Thus, these lines result from the hyperfine splitting due to two equivalent nitrogen atoms.

In the Zn:Cu powder, copper dithizonate is not involved in a slightly distorted tetrahedral lattice of zinc dithizonate. Therefore, copper(II) dithizonate is a structurally rigid coordination compound.[13] It retains its square-planar structure and does not undergo the slightest low-symmetry distortions, as evidenced by the absence of copper(II) dithizonate traces from the lattice of zinc(II) dithizonate.

A comparison of SH anisotropic parameters for three compounds (Table 2) shows that they are related to square-planar copper(II) complexes with the coordination sphere $trans$-N$_2$S$_2$.

Thus, we found that the wide lines in the EPR spectra of $Cu(HDz)_2$ solutions are not connected with low-symmetry distortions of the coordination sphere[13] because $Cu(HDz)_2$ exhibits a square-planar structure in both a solution and a solid state.

The coordination compounds of Cu^{II} usually exhibit a long time of spin–lattice relaxation, and the EPR spectral lines are narrow.

However, wide lines with poorly resolved HFS due to copper atoms were observed in solutions of hexacoordinated copper(II) complexes with monodentate ligands. This is determined by the dynamic Jahn–Teller effect, and when one Cu–ligand bond becomes stronger, the EPR line becomes sharply narrowed. This occurs when only one bidentate ligand is coordinated to copper.

On the other hand, in viscous solutions or with high-molecular-weight macrocyclic ligands, the lines of the EPR spectra of solutions are also wide, and the HFS due to copper nuclei is poorly resolved because of the effect of unresolved SH parameter anisotropy.[16]

In the other cases, the coordination compounds of copper(II), in particular, with sulfur atoms in the coordination sphere, exhibit narrow EPR lines and good resolution of SHFS due to ligand atoms.

Obviously, the above reasons for line broadening in the EPR spectra are not related to copper complexes with dithizone.

Previously,[15] it was found that tag complexes of copper(II) exhibit almost constant line widths regardless of the nature of substituents. Consequently, we can state that the spin–lattice relaxation time is not responsible for the line widths in the EPR spectra of copper complexes with dithizone. There is no answer to the question why lines due to $Cu(HDz)_2$ in solutions are broadened.

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